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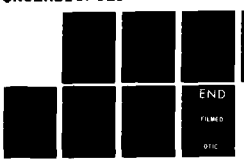

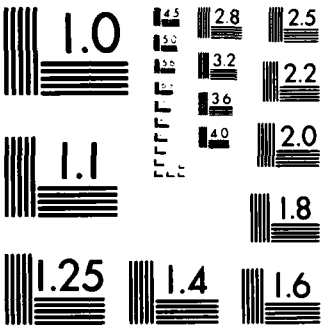

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Boron Derivatives of 3-Methylpyrazole

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The reaction of KBH_4 with Hpzme (= 3-methylpyrazole) can be directed to yield $K[H_2B(pzme)_2]$, $K[HB(pzme)_3]$, or $K[B(pzme)_4]$, respectively, depending on the experimental conditions. All three salts are stereochemically pure with the methyl group being located exclusively in the 3-position of the pyrazole ring.

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In contrast, reaction of $(CH_3)_3NBH_3$ with Hpzme yields a mixture of 1,5- and 1,7-dimethylpyrazabole. Similarly, reaction of $K[H_2B(pzme)_2]$ with $(CH_3)_3NBH_2I$ produces a mixture of 1,5- and 1,7-dimethylpyrazabole, suggesting at least two different pathways for the latter process. In addition, the compounds 4,4,8,8-tetrabromo- and 4,4,8,8-tetrakis(3-methylpyrazole-1-yl)-1,5(7)-dimethylpyrazabole were also prepared. All compounds were characterized by ^1H and ^{11}B NMR data.

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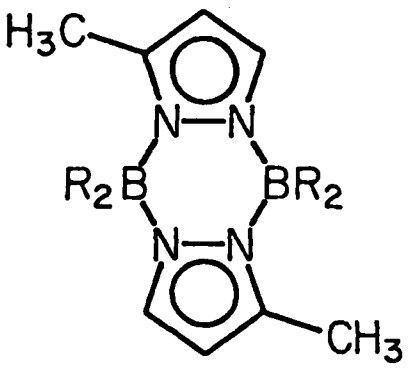
Contribution from the Department of Chemistry, University of Kentucky, Lexington, KY 40506

Boron Derivatives of 3-Methylpyrazole[1]

Kurt Niedenzu, Philipp M. Niedenzu, and Kim R. Warner

Received.....

The knowledge of boron derivatives of 3-methylpyrazole, Hpzme, is extremely limited. This lack is likely due to the mobility of the N-bonded proton in 3-methylpyrazole, the replacement of which may yield isomeric products, i.e., derivatives of either 3- or 5-methylpyrazole. Indeed, when trimethylborane was reacted with 3-methylpyrazole, the resultant pyrazabole was found to be a mixture of 1 and 2 ($R = CH_3$) in approximately 4:3 molar ratio (based on ^1H NMR data) which could not be separated.[2] Stereochemically pure 1 with $R = C_2H_5$ was obtained from the interaction of (dimethylamino)diethylborane with 1,3-dimethyl-2-(methylpyrazol-1-yl)-1,3,2-diazaboracyclohexane.[3]



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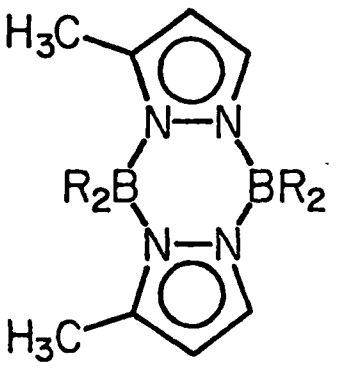

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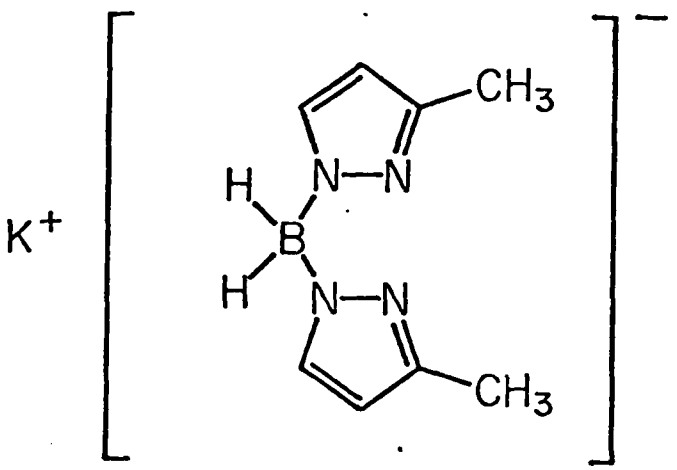
The only other known boron derivative of 3-methylpyrazole, i.e., the salt $K[H_2B(pzme)_2]$, was obtained by condensation of KBH_4 with Hpzme. Based on high-resolution ^1H NMR data, the product of this latter reaction consisted of only one isomer, 3, with the methyl group being exclusively in the 3-position of the pyrazole ring.[4]



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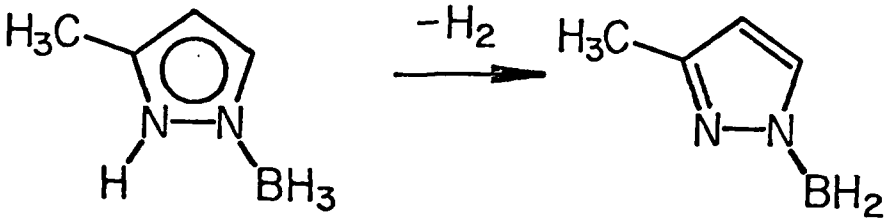
We have now found that the salts $K[HB(pzme)_3]$ and $K[B(pzme)_4]$, which are also readily obtained from the interaction of KBH_4 with Hpzme, analogously exist in only one isomeric form corresponding to 3.

As expected, reaction according to eq 1 yielded the two isomers 1 and 2 (R = H), which were obtained in approximately 3:2 molar ratio.

$$2\ \text{Hpzme} + 2\ (CH_3)_3NBH_3 \longrightarrow 2\ (CH_3)_3N + 2\ H_2 + H_2B(\mu\text{-pzme})_2BH_2 \qquad (1)$$

It seems that base displacement is the first step of the reaction. For steric reasons, this should result in the formation of 5-methylpyrazol-2-ylborane, which then loses H_2

to yield the 3-methylpyrazol-1-ylborane 4 as illustrated in eq 2.



(2)

4

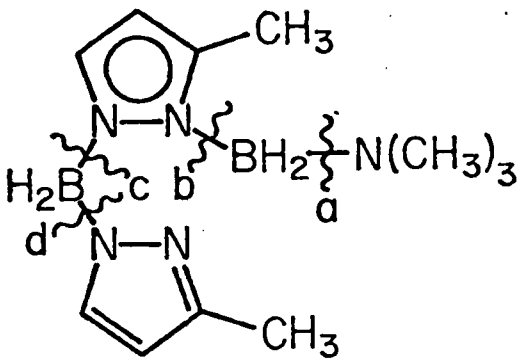
Subsequently, the dimerization of 4 to yield the pyrazabole 1 (R = H) could compete with a sigmatropic boryl group shift and following dimerization of the thus rearranged material to yield 2 (R = H). Based on the observed isomer distribution in the reaction product, the former process seems to be slightly preferred.

By fractional crystallization and sublimation it was possible to enrich mixtures of 1 and 2 (R = H) to approximately 85% of an individual species. It was found that 1 is slightly less volatile and less soluble and has the higher melting point (near 90-100 °C). ^{1}H NMR signals for 1 (R = H) are observed at $\delta(^{1}H)$ = 7.49, 6.07, 3.5* and 2.34 ppm; $\delta(^{11}B)$ = -10.5 ppm. The fraction enriched with 2 (R = H) has a melting point of 72-78 °C; NMR data for 2 (R = H): $\delta(^{1}H)$ = 7.48, 6.07, 3.5* and 2.36 ppm; $\delta(^{11}B)$ = -9.0 and -12.2 ppm. Based on the ^{11}B NMR spectral data for $(C_2H_5)_2B(\mu\text{-pzme}_2)_2BH_2$ ($Hpzme_2$ = 3,5-dimethylpyrazole),[5] the signal $\delta(^{11}B)$ = -12.2 ppm is assigned to B8 of 2, i. e., the boron atom closest to the $(C)CH_3$ groups.

Based on the structure of 3, it was hoped that the reaction according to eq 3 would proceed with the formation of only one isomer of the resultant pyrazabole, i. e., 2 (R = H).

$$3 + (CH_3)_3NBH_2I \longrightarrow (CH_3)_3N + KI + 2\ (R = H) \qquad (3)$$

However, this was not the case and only a mixture of 1 and 2 (R = H) in approximately 2:1 molar ratio was obtained. This result suggests at least two different pathways for the cited pocess. It is reasonable to assume that the first step of the overall reaction involves the formation of KI, thus providing for the neutral molecule 5.



5

There are four donor-acceptor bonds in 5 that can be broken in the transformation process to yield a pyrazabole and free trimethylamine. Cleavage of b would give the initial anion $[H_2B(pzme)_2]^-$ and the (supposedly unstable) cation $(CH_3)_3NBH_2^+$ containing trigonal boron and, thus, seems not very likely to occur; and cleavage of d would yield the $pzme^-$ anion and the cation $(CH_3)_3N(H_2)B(\mu\text{-}pzme)BH_2^+$, the latter also containing trigonal boron. Simple displacement of $(CH_3)_3N$ from 5 by the two-coordinate nitrogen of the terminal methylpyrazolyl group, i. e., cleavage of a (the anticipated

process), should lead cleanly to 2 (R = H). On the other hand, cleavage of c yields the trigonal neutral borane $H_2B(pzme)$, which is likely to dimerize to form 1 (R = H), provided the dimerization is faster than a sigmatropic boryl group shift from one pyrazol-1-ylborane nitrogen site to the other. (Sigmatropic boryl group shifts in monomeric trigonal pyrazol-1-ylboranes have been observed previously.[3,6,7]) The remaining fragment of the cleavage of c, i. e., $(CH_3)_3N(H_2)B(pzme)$, should dimerize under displacement of $(CH_3)_3N$. Since the most likely donor site would appear to be the lone two-coordinate nitrogen of the methylpyrazolyl group, this process should yield 1 (R = H). The observed isomer distribution in the reaction product clearly suggests that simple displacement of $(CH_3)_3N$ in 5 is not the most favored process. Rather, the formation of pyrazol-1-ylboranes plays a significant role in the formation of the pyrazabole.

The formation of an isomer mixture in the reaction according to eq 3 accounts for some earlier observations: The reaction of poly(pyrazol-1-yl)borates with R_2BX species (where X is a ready leaving moiety) has previously[8,9] been used for the preparation of 4,8-unsymmetrically substituted pyrazaboles. However, the yields were generally not very satisfying due to the simultaneous formation of symmetrically substituted species as byproducts. Since these reactions should also involve intermediates similar to 5, and since the present study illustrates that there are at least two reasonable pathways for the conversion of such intermediates to pyrazaboles, the

unsatisfactory yields of the desired products are readily explained. Moreover, the present data suggest the transient existence of monomeric pyrazol-1-ylboranes containing trigonal boron, even for reactions carried out at a relatively low temperature. This occurrence had previously[5] been established for high-temperature processes.

A mixture of 1 and 2 (R = H) was reacted with excess Hpzme to yield the B-pyrazolylpyrazabole $(pzme)_2B(\mu\text{-}pzme)_2B(pzme)_2$. The reaction proceeded smoothly and, as based on ^1H NMR data, the terminal pzme groups of the product are exclusively boron-bonded at the same nitrogen site, i. e., most likely forming the 3-methylpyrazol-1-yl derivative. Isomers could not be detected in the ^{11}B NMR spectrum, where only one signal at $\delta(^{11}B)$ = -0.6 ppm ($h_{\frac{1}{2}}$ = 42 Hz) was observed. Based on the digital resolution, the ^{11}B chemical shifts of the possible isomers cannot differ by more than 0.1-0.2 ppm. (Note: $\delta(^{11}B)$ of the structurally related $(pzme)_2B(\mu\text{-}pzme)_2B(pzme)_2$ is observed at -0.7 ppm.[5]) In contrast to the starting material, the ^1H NMR signal for the CH_3 groups of the bridging pzme moieties at lower field was found to be the more intensive in the product. Unless the effect of boron substitution would cause a cross-over of signals, one must asume that the isomer distribution with respect to the location of the cited groups was changed during the course of the reaction. This can be explained only by an opening of the central B_2N_4 ring during the (high-temperature) process, most likely a complete symmetrical cleavage of the pyrazabole molecule.

Reaction of a mixture of 1 and 2 (R = H) with elemental bromine gave the B-tetrabromo species. Surprisingly, the ^{1}H and ^{11}B NMR data suggest the presence of only one isomer in the product. On the other hand, this observation is disputed by the 8° melting range of the material. Presumably, the latter contains a planar B_2N_4 ring;[9-11] this event would seem to be more likely to cause an accidental overlap of the NMR signals of isomers than in species containing the B_2N_4 ring in the (more usual) boat conformation. This interpretation is supported by the fact that the ^{1}H NMR signals of the brominated pyrazabole $Br_2B(\mu\text{-pzme})_2BBr_2$ are distinctly broader than those normally observed for stereochemically pure pyrazaboles.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; all compounds gave satisfactory results. Melting points (uncorr.) were determined on a Mel-Temp block. NMR spectra were recorded on a Varian XL-200 spectrometer. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for ^{1}H, external Et_2OBF_3 for ^{11}B); an asterisk denotes a broad signal. Coupling constants J are given in Hz. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer under standard operating conditions (frequencies in cm^{-1}).

Potassium dihydrobis(3-methylpyrazol-1-yl)borate. The salt was prepared by basically following the earlier[4] procedure. When a mixture of 50 g (609 mmole) of 3-methylpyrazole and 10 g (185 mmole) of potassium tetrahydroborate had been heated to 110-120 °C for 3.5 h, an almost clear melt was obtained and hydrogen evolution had essentially ceased. A few solid particles were mechanically removed and the clear melt was poured with stirring into 150 mL of benzene. The insoluble material was collected, washed with benzene and twice with petroleum ether. After drying under vacuum, the product, 38 g (96 % yield), had a mp 217 °C (lit.:[4] 204-206 °C).

NMR data (solution in CD_3CN): $\delta(^1H)$ = 7.29 (1 H, d), 5.75 (1 H, d), 2.16 (3 H, s); $\delta(^{11}B)$ = -6.9 (t, J = 100). Additional ^1H NMR data recorded in various solvents have been reported elsewhere.[4] IR spectrum: ν(BH) = 2400-2300 (s, br).

Potassium hydrotris(3-methylpyrazol-1-yl)borate. A mixture of 10 g (185 mmole) potassium tetrahydroborate and 50 g (609 mmole) 3-methylpyrazole was slowly heated to 180-190 °C and was kept at the latter temperature for approximately 4.5 h. After that time, the essentially clear melt started to solidify. The temperature was maintained for another 45 min and the reaction was then stopped. After cooling to room temperature, the material was crushed and washed with copious amounts of benzene, then with

50 mL of petroleum ether, and was dried under vacuum to give 51 g (93 %) of a product mp 244-246 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ = 7.41 (1 H, d, J = 1.9), 5.81 (1 H, d, J = 1.7), 2.19 (3 H, s); $\delta(^{11}B)$ = -1.3 (d, J = 105). The boron-bonded H was not observed.

Potassium tetrakis(3-methylpyrazol-1-yl)borate. A mixture of 2.7 g (50 mmole) of potassium tetrahydroborate and 20 g (250 mmole) of 3-methylpyrazole was heated to maintain gentle reflux of the excess 3-methylpyrazole for 12 h. After that period of time, the mixture began to turn yellow and the reaction was stopped. The solid but moist material was crushed under benzene cover and washed with copious amounts of benzene. The colorless insoluble product was collected and dried under vacuum to give 16.9 g (90 %) of product. An analytical sample was prepared by dissolving the crude material in methanol and precipitation with dichloromethane to give an asbestos-like material, mp near 340 °C (with decomposition).

NMR data (solution in CD_3OD): $\delta(^1H)$ = 7.21 (1 H, d, J = 1.8), 5.93 (1 H, d, J = 2.1), 2.23 (3 H, s); $\delta(^{11}B)$ = +0.9 (s, $h_{\frac{1}{2}}$ = 20 Hz).

1,5(7)-Dimethylpyrazabole. A mixture of 18.25 g (0.25 mole) of trimethylamine-borane, 20.44 g (0.25 mole) of 3-methylpyrazole, and 250 mL toluene was heated to gentle reflux for 6 h. After cooling to room temperature, a small amount of gelatinous material

was filtered off and toluene was removed from the clear filtrate under reduced pressure. The remaining crude material was recrystallized from ethanol to give 16.64 g (71 % yield) of a product, melting from 68-88 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 7.29 (1 H, two overlapping unresolved d), 6.07 (1 H, two overlapping unresolved d), ca. 3.5** (2 H), 2.36 (s) + 2.34 (s) (3 H; ratio approximately 2:3); $\delta(^{11}B)$ = -9.0 (t, J = 105) + -12.2 (t, J = 105) (ca. 2 B), -10.5 (t, J = 105, ca. 3 B).

Alternate Procedure. A mixture of 7.0 g (32.7 mmole) of potassium dihydrobis(3-methylpyrazol-1-yl)borate, 6.5 g (32.7 mmole) of trimethylamine-monoiodoborane,[12] and 150 mL of toluene was heated with stirring first for 12 h at 70 °C, another 12 h at 85 °C, and finally 4 h to gentle reflux. After cooling to room temperature, the mixture was filtered and toluene was evaporated from the clear filtrate. The residue was recrystallized from ethanol to give 4.7 g (61 %) of material, mp 74-84 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 7.28 (1 H, two overlapping unresolved d), 6.07 (1 H, two overlapping unresolved d), ca. 3.5** (2 H), 2.36 (s) + 2.34 (s) (3 H, ratio approximately 1 : 2); $\delta(^{11}B)$ = -9.0 + -12.2 (ca 1 B), -10.5 (ca. 2 B). IR: ν(BH) = 2448 (ms), 2395-2340 (s, br).

1,5(5)-Dimethyl-4,4,8,8-tetrabromopyrazabole. A solution of 3.0 mL (59 mmole) of Br_2 in 15 mL of CH_2Br_2 was added dropwise to a saturated solution of 1,5(7)-dimethylpyrazabole in (ca. 15 mL) CH_2Br_2. Subsequently, the mixture was refluxed

for 30 min. On cooling to room temperature, colorless crystals of the desired compound precipitated, were collected and washed with a small amount of CH_2Br_2 and then petroleum ether, and dried under vacuum. Yield: 5.42 g (67 %), mp 249-257 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.51* (1 H, unresolved d), 6.60* (1 H, unresolved d), 2.88* (3 H, s); $\delta(^{11}B)$ = -7.4 (s, $h_{\frac{1}{2}}$ = 25 Hz).

1,5(7)-Dimethyl-4,4,8,8-tetrakis(methylpyrazol-1-yl)pyrazabole. A mixture of 9.4 g (50 mmole) of 1,5(7)-dimethylpyrazabole and 20 g (244 mmole) of 3-dimethylpyrazole was slowly heated in an oil bath. Hydrogen evolution began at a bath temperature near 130 °C. After 6 h, the temperature was slowly increased to reflux (of the excess methylpyrazole), which was maintained for 12 h. After cooling to room temperature, 50 mL of petroleum ether was added to the viscous oil and the mixture was stirred for several h to give a solid precipitate of the desried crude product. The latter was collected, dried and recrystallized from cyclohexane to give 16.2 g (64 %) of material, mp 240-242 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ of terminal pyrazolyl groups = 6.49 (1 H, d, J = 2.4), 5.72 (1 H, d, J = 2.5), 2.19 (3 H, s); of bridging pyrazolyl groups: isomer A = 7.29 (d, J = 2.4), 6.27 (d, J = 2.5), 1.79 (s); isomer B = 7.42 (d, J = 2.5), 6.55 (unresolved d), 1.72 (s), with ratio A : B ca. 2 : 1; $\delta(^{11}B)$ = -0.6 (s, $h_{\frac{1}{2}}$ = 40 Hz).

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